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Organic Chemical Reactions in Supercritical Water

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Contents

Phillip Savage is currently Professor of Chemical Engineering and Arthur F. Thurnau Professor at the University of Michigan. He received his B.S. from Penn State in 1982 and his M.Ch.E. (1983) and Ph.D. (1986) degrees from the University of Delaware. All of his degrees are in Chemical Engineering. Phil's research focuses on the rates and mechanisms of organic chemical reactions that are or may be of industrial significance. His research group uses experiments, mechanistic modeling, molecular simulation, and computational chemistry to explore different reaction systems. Most of the group's recent work has dealt with oxidation chemistry in near-critical and supercritical water. In addition to his research activities and classroom teaching at Michigan, Phil is also a co-lecturer in continuing education courses on the topics of kinetics, catalysis, and reaction engineering.

I. Introduction

Water near or above its critical point (374 °C, 218 atm) is attracting increased attention as a medium for organic chemistry. Most of this new attention is driven by the search for more “green” or environmentally benign chemical processes. Using near-critical or supercritical water (SCW) instead of organic solvents in chemical processes offers environmental advantages and may lead to pollution prevention. Interest in doing chemistry in SCW is not entirely new, however. There has been much previous research in this area with applications in synthetic fuels production, biomass processing, waste treatment, materials synthesis, and geochemistry.

Water near its critical point possesses properties very different from those of ambient liquid water. The dielectric constant is much lower, and the number and persistence of hydrogen bonds are both diminished. As a result, high-temperature water behaves like many organic solvents in that organic compounds enjoy high solubilities in near-critical water and complete miscibility with SCW. Moreover, gases are also miscible in SCW so employing a SCW reaction environment provides an opportunity to conduct chemistry in a single fluid phase that would otherwise occur in a multiphase system under more conventional conditions. The advantages of a single supercritical phase reaction medium are that higher concentrations of reactants can often be attained and that there are no interphase mass transport processes to hinder reaction rates.

The ion product, or dissociation constant (K_w) for water as it approaches the critical point, is about 3 orders of magnitude higher than it is for ambient liquid water. Accordingly, in addition to near-critical and supercritical water being an excellent solvent for organic compounds, it can also boast a higher H^+ and OH^- ion concentration than liquid water under certain conditions. As such, dense high-temperature water is an effective medium for acid- and base-catalyzed reactions of organic compounds. In fact, the dissociation of water itself near the critical point generates a sufficiently high H^+ concentration that some acid-catalyzed organic reactions proceed without any added acid (see sections II.B and II.D for examples). As one exceeds the critical point, however, K_w decreases dramatically. For example, K_w is about 9 orders of magnitude lower at 600 °C and about 250 atm than it is at ambient conditions. SCW in this

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high-temperature, low-density region is a poor medium for ionic chemistry.

Another difference between the properties (e.g., viscosity, dielectric constant, K_w) of SCW and ambient liquid water is that they vary continuously over much larger ranges in the supercritical state. This variation offers the possibility of using pressure and temperature to tune the properties of the reaction medium to optimal values for a given chemical transformation.

As its title indicates, this review focuses on organic chemical reactions in supercritical water. The primary emphasis is on chemical transformations and reaction chemistry. Accordingly, reaction pathways, products, kinetics, and mechanisms claim center stage. This review does not cover molecular modeling studies or simulations of reactions in SCW. Such computational work[1-8] usually considers a well-characterized reaction, and the aim is to better characterize local solvation effects in SCW. As such, one learns much about the physics of SCW solutions, but gains little new insight into reaction chemistry in SCW. Further, we also exclude studies[9-15] of acid–base reactions and equilibria in SCW. Reactions involving entirely inorganic compounds are also excluded, which means that the field of hydrothermal materials synthesis and processing is not covered. Reactions at subcritical conditions are generally excluded except for some particularly significant work on reactions in near-critical water, especially as it relates to chemical synthesis. Finally, this review is based entirely on a search of the archival, peer-reviewed chemical literature. We made no attempts to include work appearing exclusively in nonrefereed conference proceedings, dissertations, government reports, or patents.

Our earlier review[16] on reactions at supercritical conditions (all fluids, not only water) covered the field up to June 1994, so the present review begins with work published around this date. This decision to limit the present review to work published in 1994 or later meant that many important earlier investigations have been excluded. Therefore, to get a complete account of research in this field, one needs to refer to the earlier review[16] and the references therein along with the present review.

Although only four years have elapsed since that comprehensive review was submitted, the field of reactions in SCW has grown substantially. New articles dealing with chemistry in near-critical and supercritical water appear at an ever increasing rate. Evidence to this end was obtained from the Science Citation Index. A general search was performed using "supercritical" and "water" as the key words, and then we examined each article to assess whether it dealt with chemical reactions. Figure 1 summarizes the results by showing the number of articles on chemical reactions in SCW per year since 1987. Of all the articles published in this field in the last 11 years, over half have appeared since 1995.

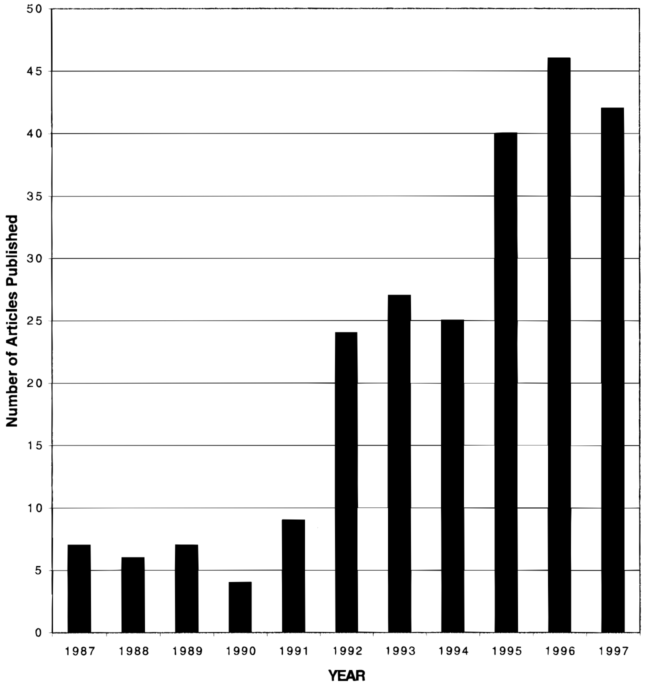

Figure 1. Number of articles on reactions in SCW published each year since 1987.

This review is organized around two major themes: chemical synthesis and chemical conversion. The former topic deals with deliberate attempts to use SCW as a medium for forming specific chemical bonds or introducing specific functional groups into molecules. The latter topic focuses on the more numerous studies revealing the kinetics, products, and pathways associated with a given chemical system in SCW. The articles categorized as chemical synthesis tend to ask and answer the question "how can one accomplish specific chemical transformations in SCW?" and the articles categorized as chemical conversion tend to ask and answer "what happens to this compound in SCW?". The chemical synthesis articles tend to be product-oriented, whereas the chemical conversion articles are more reactant-oriented.

II. Chemical Synthesis

Water near its critical point can serve as an environmentally benign solvent, a reactant, and a catalyst in organic chemical reactions. These different aspects of a SCW reaction medium have been exploited for the purpose of conducting chemical syntheses. Parsons,[17] Katritzky et al.,[18] An et al.,[19] and Simoneit[20] provide very good overviews of the types of synthetic organic chemistry that have been demonstrated in near-critical and supercritical water. We summarize key results from previous studies here, and we take the liberty of including several accounts of organic syntheses in subcritical water instead of focusing exclusively on the more limited literature dealing with supercritical water.

A. Hydrogenation/Dehydrogenation

Crittendon and Parsons[21] showed that late transition metal complexes are active dehydrogenation catalysts in SCW. In the presence of a PtO_2 catalyst, cyclohexanol was dehydrogenated via two parallel paths. One path involved dehydrogenation of the ring, and the other path involved oxidation of the alcohol group to the corresponding ketone. Metallic platinum was shown to be the catalytic species for alcohol oxidation, so metallic platinum must have formed in situ from the PtO_2 initially loaded in the reactor. Aromatization of the cyclohexyl ring also occurred in these experiments. Benzene was the major product from the reactions of cyclohexane, cyclohexene, and cyclohexanol in SCW in the presence of a PtO_2 catalyst. Addition of HCl to the reactor essentially closed the aromatization path, whereas addition of NH_4OH simply suppressed aromatization but still allowed it to proceed. In addition, the presence of NH_4OH in the system shifted the product distribution from cyclohexanol such that cyclohexanone was the major product. Low yields of phenol, apparently from dehydrogenation of cyclohexanone, were also observed. These important experiments showed that one can control the functional group transformations and the extent of dehydrogenation by judicious selection of catalysts and pH in SCW.

Adschiri et al.[22] used a SCW reaction medium and a conventional $NiMo/Al_2O_3$ hydrotreating catalyst to hydrogenate and remove sulfur from dibenzothiophene. They obtained higher conversions in CO−SCW and HCOOH−SCW media than in a H_2−SCW reaction medium. The authors concluded that the water−gas shift reaction was occurring in the CO− and HCOOH−SCW media, and that it produced chemical species that hydrogenate dibenzothiophene more effectively than H_2 gas. This research showed that hydrodesulfurization can be achieved without the addition of expensive H_2 gas, as is currently practiced industrially.

B. C–C Bond Formation

Much of the work on using near-critical and supercritical water as a medium for chemical synthesis has investigated ways to form (and break) selected carbon−carbon bonds. For example, Friedel−Crafts alkylation reactions have been accomplished[18,23] in high-temperature water. Both phenol and *p*-cresol were successfully alkylated with *tert*-butyl alcohol and 2-propanol at 275 °C in the absence of any added acid catalyst to produce sterically hindered phenols.[23] Thus, water served as both the solvent and the catalyst for these alkylation reactions. Reaction times ranged from about 1 h to over 100 h for the different reactant systems.

Parsons and co-workers[24,25] have reported extensive work on palladium-catalyzed alkene−arene coupling reactions in near-critical and supercritical water. These reactions can be classified as Heck arylation reactions. Figure 2 shows the catalytic cycle for coupling iodobenzene with an alkene. The reactions in high-temperature water were similar to those observed in traditional organic solvents, but they were more sensitive to steric effects and the nature of the alkene. One can also take advantage of the rapid elimination reactions (discussed in more detail in section II.E) that some compounds undergo in SCW to generate in situ the alkene needed for coupling.[25] Alcohols, halides, and carboxyl groups are all rapidly eliminated to generate compounds with double bonds. For example, 2-phenylethanol dehydrates to form styrene, which can then couple with an arene. Thus, a larger suite of starting compounds can be used in Heck coupling reactions in SCW.

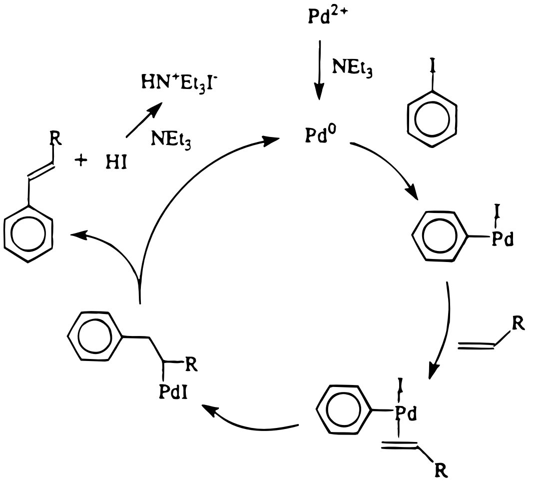

Figure 2. Catalytic cycle for Heck coupling reaction (in organic media). (Reprinted from ref 24. Copyright 1995 American Chemical Society.)

Diels−Alder cycloaddition reactions have also been conducted in SCW.[26] Several different diene/dienophile combinations have been explored. Aldol condensation reactions can also be accomplished in high-temperature water. 2,5-Hexanedione is unreactive in pure water, but in the presence of a small amount of base (NaOH) this dione underwent an intramolecular aldol condensation to form 3-methylcyclopent-2-enone in 81% yield.[19] Parsons[17] and An et al.[19] also give other examples of cyclization reactions.

Carbon−carbon bond cleavage reactions can also occur in near-critical and supercritical water. Kuhlmann et al.[27] obtained rapid and irreversible ring opening of 2,5-dimethylfuran to produce 2,5-hexanedione quantitatively at 250 °C. The reaction was acid-catalyzed.

C. Rearrangements

Kuhlmann et al.[28] report that pinacol and two different bicyclic diols underwent quantitative rearrangement to the corresponding ketones in pure water at 275 °C. The potential side reaction of elimination led to negligible alkene formation. Crittendon and Parsons[21] report that cyclohexene rearranged reversibly to methylcyclopentene in SCW in the presence of a mineral acid or acidic metal salts. This ring contraction was attributed to acid catalysis and the rearrangement of a carbocation. An et al.[19] showed that Claisen, Rupe, and Meyer-Schuster rearrangements are also operative in pure water at elevated temperatures.

D. Hydration/Dehydration

Antal and co-workers have been pioneers in studying the dehydration of alcohols to olefins in near-critical and supercritical water. Their most recent work[29,30] in this area centers around *tert*-butyl alcohol. They found that the conversion of *tert*-butyl alcohol to isobutylene was rapid and selective in near-critical water at temperatures around 250 °C. The

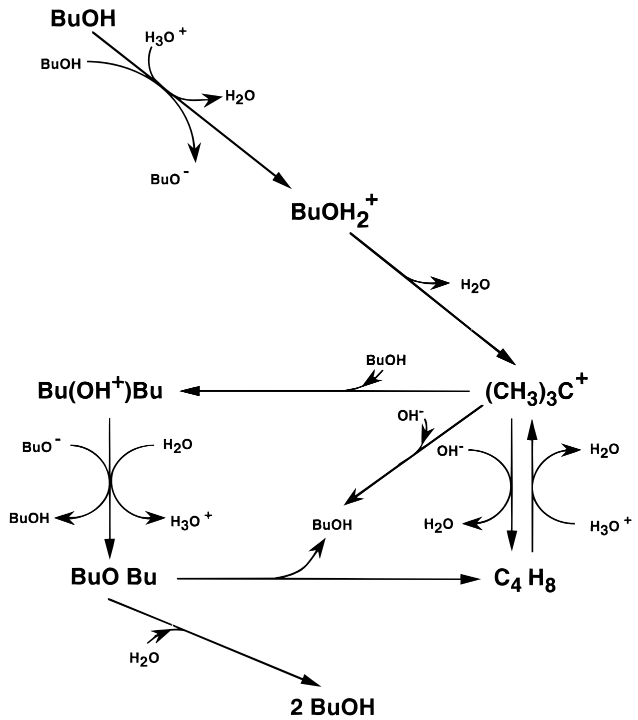

Figure 3. Acid-catalyzed reactions of *tert*-butyl alcohol in high-temperature water. (Reprinted from ref 30. Copyright 1997 American Chemical Society.)

reaction occurs even in the absence of added acid or base, but the addition of H_2SO_4 or NaOH did accelerate the reaction rate. In the absence of added acid, hydronium ions formed by the dissociation of water are the primary catalytic agents. A reaction mechanism and kinetics for each elementary step were also reported. Figure 3 shows the main reaction steps for this dehydration reaction.

The dehydration of other alcohols, such as cyclohexanol,[21,27] 2-methylcyclohexanol,[27] and 2-phenylethanol[25] have also been reported, but there is much less quantitative and mechanistic information available for these compounds. Several different mineral acids and acidic metal complexes as well as NH_4OH are effective catalysts for dehydration.

If alcohols undergo dehydration to form alkenes in water near its critical point, then the reverse reaction, addition of water across a double bond should also be operative, although chemical equilibrium would be a limiting factor. Crittendon and Parsons[21] obtained low yields of cyclohexanol from cyclohexene hydration in SCW. The reaction required added PtO_2 and acid or base catalyst. An et al.[19] report hydration of some olefins without an added catalyst, but at lower temperatures around 250 °C. They also confirmed earlier work that alkynes can be converted to the corresponding ketones by the addition of water.

E. Elimination

One type of elimination reaction, dehydration, has already been discussed. In this section we briefly consider other elimination reactions documented in SCW. Carboxylic acids undergo facile decarboxylation in pure, high-temperature water, as evidenced by reports regarding formic acid,[31] citric and itaconic acids,[32] and cinnamic and indole-2-carboxylic acid.[19] For example, Carlsson et al.[32] show that citric acid can be converted in high yields to methacrylic acid in high-temperature water through sequential dehydration and decarboxylation reactions. Figure 4 shows the reaction pathways they postulate for these various chemical transformations.

Dehydrohalogenation reactions are also rapid, as evidenced by the reported behavior of poly(vinyl chloride)[18] and methylene chloride.[33] Trichloroacetic acid decomposition provides an example of both decarboxylation and dehydrochlorination. This compound decomposed completely to HCl, CO, CO_2, and H_2 in SCW at 600 °C and 65 s reaction time.[34] Hydrolysis was thought to be at least partially responsible for the conversion. More details and more examples of elimination reactions in SCW appear later in this review in section III.A.2.

F. Hydrolysis

As summarized by An et al.[19] and Katritzky et al.[18] several different compounds readily hydrolyze in SCW. Esters, for example, can undergo an autocatalytic hydrolysis to form carboxylic acids and alcohols. The acid produced catalyzes the hydrolysis, and this feature is the source of the autocatalysis. Nitriles also undergo hydrolysis to form the corresponding amide and then further hydrolysis to the corresponding acid. Iyer and Klein[35] provide a thorough kinetics study of butyronitrile hydrolysis. They observed autocatalytic kinetics, consistent with the acid product catalyzing further hydrolysis reactions. They also reported on the effect of pressure on the hydrolysis rate and used their data to calculate the effective activation volumes. Hydrolysis in high-temperature water is an effective and efficient means of decomposing some synthetic polymers. For example, poly(ethylene terephthalate) and polyurethane foams can be hydrolyzed to reusable diacids and glycols and diamines and glycols, respectively.[18] Activated diaryl ethers undergo hydrolysis to form the corresponding hydroxyarenes.[18]

G. Partial Oxidation

Economically converting methane to oxygenates or higher hydrocarbons that are less expensive to liquefy and transport has been an elusive goal in the chemical community for several years. Chemistry that gives high yields of the target compound would allow use of vast methane reserves in remote locations. It is in this context that partial oxidation of methane in SCW around 400 °C has been examined as a potential route to methanol. These investigations have explored both homogeneous[36,37] free-radical reactions and heterogeneous catalytic[38] reactions. High selectivities to oxygenates were obtained, but only at very low methane conversions. As a result, the highest methanol yields observed were only about 1%. Our analysis revealed that a large-scale chemical process based on this chemistry and this highest yield would not be profitable. Unless much higher methanol yields can be obtained, partial oxidation in SCW does not appear to be an economically viable route for converting methane to methanol.

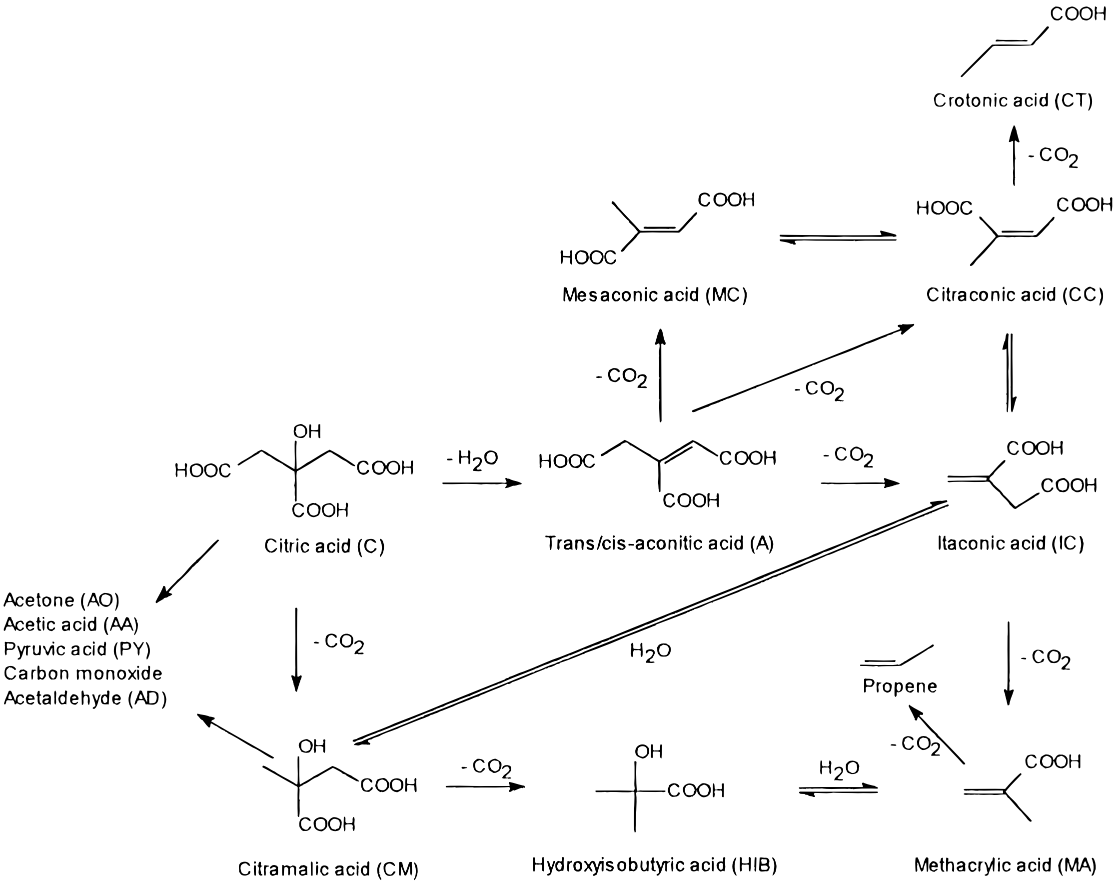

Figure 4. Reaction network for decomposition of citric acid in high-temperature water. (Reprinted from ref 32. Copyright 1994 American Chemical Society.)

The catalytic partial oxidation of alkylaromatics in near-critical water (around 300−350 °C) to produce aldehydes, ketones, and acids has also been explored.[39] The precise products and their yields are strong functions of the reaction conditions and the specific catalyst employed. For example, *p*-xylene can be converted to terephthalic acid in 64% yield with a $MnBr_2$ catalyst, but the major products are *p*-tolualdehyde and *p*-toluic acid, both in 24% yield when $Co(OAc)_2$ is the catalyst. Similarly, toluene can be converted to a 63% yield of benzoic acid under one set of reaction conditions, but to benzaldehyde (30% yield) and less benzoic acid (10% yield) using a different catalyst, less oxygen, and a shorter reaction time. All of these experiments were done in nonisothermal, batch reactors so no kinetics information is available. Nevertheless, the results clearly show the potential utility of near-critical water as a medium for partial oxidation reactions.

H. H–D Exchange

Some compounds undergo hydrogen atom exchange reactions with water at high temperatures and pressures. Kuhlmann et al.[27,28] have investigated the behavior of several different organic compounds in subcritical D_2O to determine the kinetics of H−D exchange. Simple alcohols do not participate in hydrogen exchange reactions, whereas the α positions of ketone carbonyl groups (e.g., CH_3 groups in acetone) undergo rapid and nearly complete exchange. Evilia and co-workers[40−43] and Junk et al.[44] showed that supercritical D_2O with added base is an excellent medium for H−D exchange in amino acids, very weak organic “acids”, and anilines. Reaction with supercritical D_2O provides a convenient alternate route to the synthesis of deuterated organic compounds. Deuterium was also present in the products formed from *tert*-butylbenzene pyrolysis[45] and polymer cracking[46] in supercritical D_2O. These experiments clearly show that near-critical and supercritical water is not merely a solvent, but rather also a reactant, at least in hydrogen exchange reactions.

III. Chemical Conversion

This section is apportioned into two subsections, decomposition and oxidation. The decomposition subsection discusses the chemical behavior of different classes of compounds in SCW, and at times in the presence of catalysts or other additives such as NH_3, dihydroanthracene, formic acid, and formate ion. The oxidation subsection describes recent research into total oxidation reactions in SCW.

A. Decomposition

This section focuses on the decomposition of organic compounds and materials in SCW in the absence of oxygen. We first describe work dealing with complex materials such as tires, polymers, vegetable oils, and biomass. Next we outline recent work on the reactivity of different types of individual compounds and functional groups in SCW, both pure and with additives.

1. Complex Materials

Supercritical water has been explored as a medium for the degradation of waste synthetic polymers.[46−51] Rubber tires were converted to a 44% oil yield by reaction in SCW at 400 °C.[50] Polystyrene-based ion-exchange resins were subjected to SCW at 380 °C for 1 h.[49] Less than 5% of the polymer decomposed, and the products included styrene and several oxygenated arenes such as acetophenone and benzaldehyde.

Water above its critical temperature was used to extract oil and oil precursors from oil shale.[52] Although nominally termed extraction, this treatment certainly involved cleavage of chemical bonds in the oil shale. Processing in SCW, and especially with added CO, led to hydrocarbon yields higher than those obtained from more conventional pyrolytic treatment.

Holliday et al.[53] report that water near its critical point is a good medium for the hydrolysis of triglyceride-based vegetable oils into their fatty acid constituents. A process based on this chemistry might be faster than conventional processes and also give a product free of catalyst residues. Conditions below the critical point appeared to be most favorable because undesired degradation, pyrolysis, and polymerization reactions occurred at the higher supercritical temperatures.

The allure of using biomass as a renewable source of fuels or chemicals and the knowledge that cellulose, a major component of biomass, can be hydrolyzed to produce glucose and other products has prompted several recent studies into the decomposition of cellulose,[54,55] glucose, and related compounds in near-critical and supercritical water. Holgate et al.[56] examined glucose hydrolysis at temperatures between 425 and 600 °C and for residence times around 6 s. These reaction conditions led to glucose conversions of 97% or higher in all experiments. Thus, Holgate et al. were not able to determine the reaction kinetics. They did find that the product distribution was sensitive to temperature. At the lower temperatures the gas yield was low, and most of the decomposition products were liquid phase, lower molecular weight compounds such as acetic acid, acetonylacetone, and acetaldehyde. At the higher temperatures, the gas yield was essentially 100%, and the main components were H_2 and CO_2 in 1.7 to 1 molar ratio. This result was consistent with previous work showing that glucose can be completely gasified by reactions in supercritical water.

Kabyemela et al.[57−60] performed a more extensive complementary study at much milder conditions (T = 300−400 °C, τ = 0.02−2.0 s) where the kinetics and primary reaction networks were accessible. They also examined the effect of pressure on the reaction rates. Their experiments included glucose, cellobiose (a disaccharide of glucose), and the glucose decomposition products dihydroxyacetone and glyceraldehyde, as reactants. By investigating the reactions of a variety of starting materials they were able to assemble the reaction network in Figure 5, which summarizes the various chemical conversions occurring in water near its critical point. Cellobiose decomposes both thermally (k_1 and k_2) and hydrolytically (k_H) to form the products shown. Glucose interconverts to fructose (k_{GF}) or it decomposes to the products shown. Interestingly, high yields of erythrose can be obtained from glucose in supercritical water.[59] The authors reported a selectivity of nearly 80% at a glucose conversion of 50%. Erythrose is a useful chemical in the food, fine chemicals, and pharmaceutical industries.

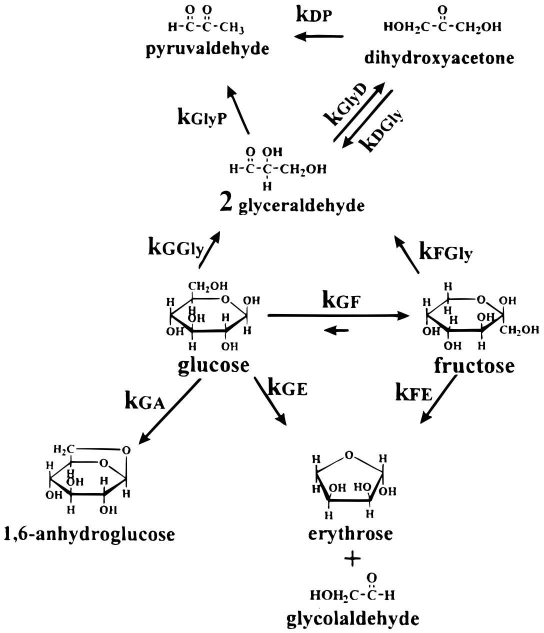

Figure 5. Glucose decomposition pathways in SCW. (Reprinted from ref 60. Copyright 1998 American Chemical Society.)

Xu et al.[61] explored the activity of various charcoals and activated carbons as biomass gasification catalysts in SCW. Catalysts are required to achieve complete gasification of concentrated feedstocks (>20 wt % organics in water). Complete gasification of different feedstocks was achieved at 600 °C, and H_2, CO, CO_2, and CH_4 were the major components of the gases. Hydrogen production is the goal of gasification, so the abundance of CO and CH_4, which could have reacted further to produce more H_2 by the water−gas shift reaction and re-forming, was not desired.

In a follow-up study, Matsumura et al.[62] gasified a granular activated carbon in SCW around 600 °C. The gas was primarily H_2 and CO_2 in a 2:1 molar ratio, with much smaller amounts of methane and CO. They found that the kinetics at supercritical conditions were in agreement with rates measured for carbon gasification in steam at ambient pressures, which indicated that the kinetics were largely insensitive to pressure.

A team at the Pacific Northwest National Laboratory[63−67] has done extensive research and development work on chemical processing in near-critical water. They report a process whereby a wide variety of organic compounds and lignocellulosic materials can be catalytically converted to a methane-rich, medium-BTU fuel gas at temperatures around 350 °C for reaction times around 10 min. Processing highmoisture biomass in an aqueous environment means there is no need for the costly dewatering or drying pretreatment steps that accompany other conversion schemes. This process can also be used to destroy organic wastes.

2. Individual Organic Compounds

The reactivities of a large number of different organic compounds in SCW have been determined. Most of these studies were motivated by a desire to understand the effect of SCW processing on some other more complex material, such as biomass, coal, oil shale, sludges, military wastes, or wastewater components. Katritzky et al.[18] provide an overview of largely their own work in this field through 1995, and Savage et al.[16] provide a more comprehensive review of the pre-1994 research.

a. Hydrocarbons. Biphenyl, 1,1′-binaphthyl, diphenylmethane, 1-benzylnaphthalene, naphthalene, and phenanthrene are resistant to significant reaction in pure SCW at 460 °C for up to 1 h.[47,68,69] Other polycyclic arenes[70] likewise exhibited conversions of only a few percent, with the main products being hydroarenes. Hydrocarbons with weaker bonds (e.g., *tert*-butylbenzene, benzylcyclohexane, benzyl tetralin, hexylbenzene, 1-decylnaphthalene, cyclohexylbenzene, and cyclohexylnaphthalene) did undergo decomposition in SCW at $T \geq 460$ °C, and the reaction paths in SCW are similar to those in a hydrocarbon solvent.[45,69] Free-radical chemistry is almost certainly responsible. Water does not appear to be either a reactant (i.e., a means of incorporating oxygen functionalities into the hydrocarbons) or catalyst for these compounds. As noted earlier in this review, however, proton exchange reactions between hydrocarbons and water can certainly occur. These reports are fully consistent with the previous work in the field related to hydrocarbon pyrolysis in SCW.[16]

b. Nitrogen-Containing Compounds. Iyer and Klein have conducted detailed studies of the reactions of 1-nitrobutane[71] and butyronitrile[35] in pure high-temperature water. As shown in Figure 6, nitrobutane undergoes parallel transformations to butanal and butyronitrile. Butyronitrile is hydrolyzed to butanamide, which then hydrolyzes further and loses NH_3 to form butyric acid. Butanal can be converted to butanol, which can undergo a condensation reaction with butyric acid to form butyl butyrate. Kinetics and mechanisms for several of the chemical transformations are proposed.

Wang et al.[72] provide a thorough examination of the kinetics, reaction networks, and possible mechanisms of the reactions of six different nitroanilines in water at 300 °C. 2-Nitroaniline formed benzofurazan as the major primary product. 4-Nitroaniline formed 4-aminoaniline as the major product. The reactions in water were 4−8 times faster than decomposition via neat pyrolysis under otherwise identical conditions. Additionally, the presence of

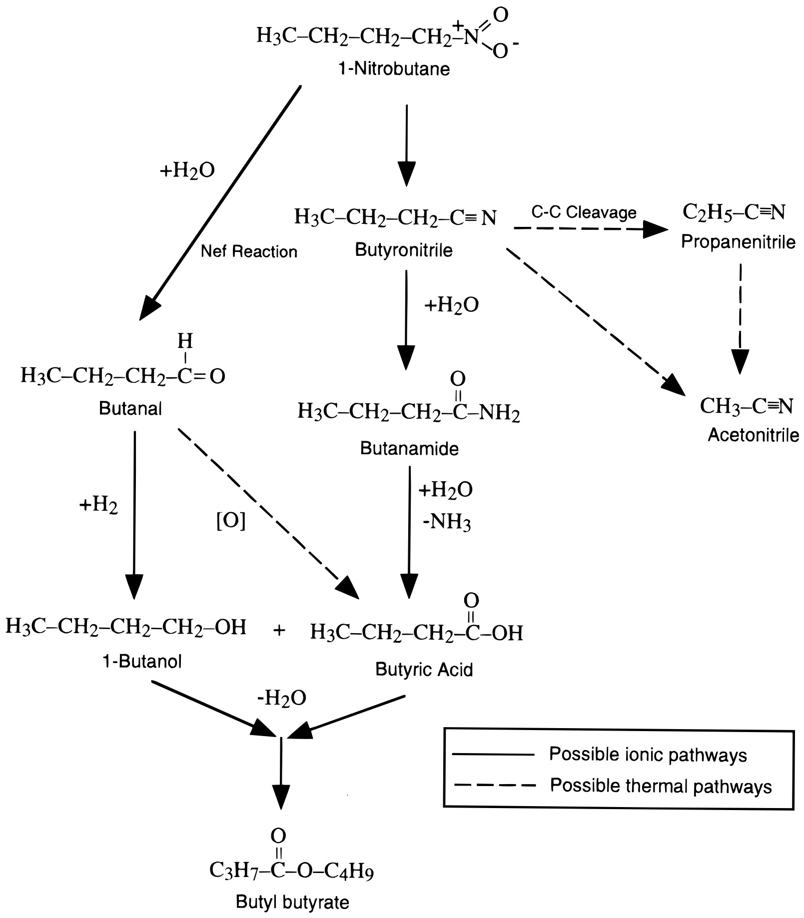

Figure 6. Reaction network for the conversion of 1-nitrobutane in high-temperature water. (Reprinted with permission from ref 71. Copyright 1996 PRA Press.)

high-temperature water also influenced the product distribution.

Lee and co-workers examined the decomposition of nitrobenzene[73] and 4-nitroaniline[74] in supercritical water. Nitrobenzene decomposed even in the absence of oxygen, and a global rate law was reported. The main products were benzene and nitrite, along with some CO and CO_2. Decomposition of 4-nitroaniline[74] in the absence of added oxygen followed first-order kinetics. NH_3, CO, CO_2, and N_2 were among the products formed.

4-Nitrotoluene decomposed in SCW to form small amounts of aniline, 4-toluidine, and toluene, but much higher yields of tar/char.[75] The addition of dihydroanthracene (a hydrogen donor) or NH_3 enhanced the yields of aniline and 4-toluidine. The addition of $ZnCl_2$ promoted the formation of phenol and 4-cresol, at the expense of aniline and 4-toluidine. Similar effects of additives were observed for the decomposition of 4-toluidine in SCW.

All of the other recent work on the behavior of nitrogen-containing compounds in pure SCW has focused less on the kinetics and more on product identities and differences therein for reactions with different additives. Quinuclidine $[CH(CH_2CH_2)_3N]$ formed alkylpyridines in SCW at temperatures around 425 °C.[75] 3-Phenylpyridine was less reactive than quinuclidine, and alkylbenzenes and tars were the major products. The addition of $ZnCl_2$ led to complete removal of the organic nitrogen as NH_3.

Katritzky et al.[76,77] examined the reactivity of several heterocyclic nitrogen-containing compounds in SCW at 460 °C for up to 60 min of exposure. Pyridine, indole, and carbazole are essentially unreactive in pure SCW at 460 °C for up to 60 min.[76] Acridine and phenanthridine are also largely stable under these conditions, with only small amounts of dihydroacridine and dihydrophenanthridine, respectively, being formed. Both 1,2,3,4- and 5,6,7,8-tetrahydroquinoline underwent dehydrogenation to form quinoline in 5.1% and 6.1% yields, respectively. 2,3-Dimethylindole and 1- and 2-methylindole underwent demethylation and methylation reactions, with conversions of only a few percent at 460 °C and 60 min. Similar behavior was observed for pyrrole, 2,5-dimethylpyrrole, and 2,4,6-trimethylpyridine. 4-Propylpyridine produced primarily smaller alkylpyridines. 1,2,3,4-Tetrahydrocarbazole was more reactive. The main reaction paths are dehydrogenation to carbazole and ring opening to produce methylindoles. 2-Aminobiphenyl[70] underwent 15% conversion in pure SCW after a 1-h reaction. 9*H*-Carbazole, formed via ring closure, was the major reaction product. Biaryl nitrogen-containing compounds (2-phenylpyridine, 2-(1-naphthyl)pyridine, 2-phenylquinoline, 2-(1-naphthyl)quinoline, and 2-phenylindole) are essentially stable in SCW at 460 °C for up to 1 h.[68] Water itself does not affect the reaction paths for these heterocyclic nitrogen-containing compounds. The addition of formic acid or sodium formate, however, results in the reduction of the aromatic rings and cleavage of biaryl bonds in many of the compounds. These hydrogenation reactions were not as prevalent for non-nitrogen-containing heterocycles.

Olobunmi and Berkowitz[78] reexamined the decomposition of quinoline and isoquinoline in SCW. In pure water at 400 °C, both compounds are stable for up to 48 h. Katritzky et al.[76] also found that these compounds, along with 2-methylquinoline, underwent less than 3% conversion at 460 °C for 60 min. In the presence of added Fe_2O_3, however, quinoline produced *o*-xylene, benzeneamines, and aniline in the highest yields.[78] Iso-quinoline was less reactive, and it produced ethylbenzene, xylene, and other dialkyl-substituted benzenes. CO_2 was the most abundant gaseous product from both compounds. The formation of these products indicates that SCW served as an oxidant (to form CO_2) and perhaps as a hydrogen donor. The authors attributed at least a portion of the chemistry to ionic reactions involving H^+ or OH^-.

c. Sulfur-Containing Compounds. There appears to have been no kinetics studies of the decomposition of sulfur-containing compounds in SCW within the last four years, although studies of this type have been reported in the more distant past.[16] The recent work[75,78,79] that has been completed is largely descriptive. The behavior of selected compounds is examined in SCW and often compared with the behavior observed in the absence of water, or in water with additives, or in a hydrocarbon solvent.

Benzyl sulfide reacts completely within 30 min in SCW at 400 °C to form benzene and toluene as the major volatile products.[75] Thianaphthene is more stable in pure SCW,[79] and a $ZnCl_2$ catalyst or NH_3 were required to achieve appreciable desulfurization.[75] An Fe_2O_3 catalyst was also effective,[78] but to a lesser degree. Thianthrene produces dibenzothiophene as the exclusive product.[78] Katritzky et al.[79] report on the behavior of nine other sulfur-containing compounds in SCW at 460 °C. Thiophene, benzothiophene, and diphenyl sulfide were all essentially unreactive in pure SCW under the conditions investigated. Thiophenol reacted to give nearly quantitative yields of diphenyl sulfide, apparently via a reversible reaction that reached equilibrium within a few minutes. 1-Naphthalenethiol reactions were analogous to those of thiophenol. Cyclohexyl phenyl sulfide produced 1-methylcyclopentene and thiophenol in nearly equal yields. The 1-methylcyclopentene was attributed to acid-catalyzed cleavage of the sulfide and rearrangement of the cyclohexyl fragment. Results for 1-naphthyl phenyl sulfide, 1-phenylthiotetralin, dioctyl sulfide, and tetrahydrothiophene are also available. Siskin et al.[68] report that 2-arylthiophenes and 2-aryl-benzothiophenes (2-phenylthiophene, 2-(1-naphthyl)thiophene, 2-phenylbenzo-[*b*]thiophene, and 2-(1-naphthyl)benzo[*b*]thiophene) exhibit low reactivity in pure SCW at 460 °C for 1 h. Cleavage of the biaryl bond can be achieved by reaction in the presence of added sodium formate, however, which produces basic reaction conditions. Katritzky et al.[79] also report on how the product distributions shift as different additives (formic acid, sodium formate, sodium carbonate, phosphoric acid) were included in the reactors. Adding formic acid, for example, enhances acid-catalyzed reactions and produces reducing reaction conditions. Formic acid is also thought to be an intermediate in the water–gas shift reaction, so its addition simulates the CO/H_2O treatment of hydrocarbons, which is often used in fuel processing studies.

d. Oxygen-Containing Compounds. Martino and Savage[80] report kinetics and products from the decomposition of cresols, hydroxybenzaldehydes, nitrophenols, and benzenediols in supercritical water at 460 °C for times on the order of 10 s. These conditions are representative of those encountered in the supercritical water oxidation process (discussed later in section III.B in this review). They found that the cresols are largely stable under these conditions and that hydroxybenzaldehydes and nitrophenols are reactive. Phenol was formed in high yields and with nearly 100% selectivity from all three hydroxybenzaldehyde isomers. Phenol was also the only product consistently present in high yields from decomposition of nitrophenols. The authors also observed that for a given substituent position, nitrophenols were more reactive than hydroxybenzaldehydes, which were more reactive than cresols. For a given substituent, the ortho isomer of the substituted phenol was the most reactive in SCW.

The reactions of dibenzyl ether in SCW were recently reexamined[81] in an effort to expand the kinetics database for the competing parallel hydrolysis and pyrolysis paths. The hydrolysis path leads to benzyl alcohol and the pyrolysis path leads to benzaldehyde and toluene as primary products. The authors determined the kinetics for these paths and others in the reaction network.

Formic acid decomposes rapidly in SCW via two parallel paths, decarboxylation and dehydration.[31] The major products are CO_2 and H_2 from the decarboxylation path, but small amounts of CO (and presumably H_2O) are also formed, from the dehydration path. First-order kinetics provides a good description of the transformations, and rate constants for the two paths are available for decomposition at different temperatures and pressures. Water appears to be a catalyst in formic acid decomposition because the rates in SCW are faster than in the gas phase. Additionally, water shifts the product spectrum so that decarboxylation is the faster path, whereas dehydration is faster in the gas phase. This catalytic role of water molecules was confirmed through ab initio quantum chemical calculations,[82] which showed that the presence of water molecules permitted formation of lower energy transition states.

Katritzky et al.[69,70] report on the reactions of several oxygen-containing compounds in pure SCW at 460 °C and for either 7 or 60 min of exposure. 1-Naphthol underwent 16% conversion after 60 min, and 1,1′-binaphthyl ether was the sole product. 1-Octanol underwent 5% conversion after 7 min, and the major products were octanal, octene, and heptene. Benzophenone, 9-fluorenone, anthraquinone, acridone, 3,4-benzocoumarin, and 2-phenylphenol exhibited conversions of at most a few percent upon treatment in pure SCW for up to 1 h.[70] Phenanthrenequinone was completely converted after 1 h in 460 °C SCW. The main product is 9-fluorenone, apparently formed via decarbonylation. 1,4-Naphthoquinone is also very reactive under these conditions. 1-Naphthyl phenyl ether[69] hydrolyzed after 1 h in SCW to form phenol and 1-naphthol in about 10% yield. Diphenyl ether and dibenzofuran were both stable under these conditions. Cyclohexyl phenyl ether, on the other hand, was completely converted after 7 min of reaction time. Figure 7 shows the reaction network. The major products are phenol and 1-methylcyclopentene, presumably formed from acid-catalyzed cleavage of the C–O bond and subsequent rearrangement of the cyclohexyl cation to form methylcyclopentene. In this case, water (or more precisely H^+ derived from water) serves as the catalyst. Phenol and cyclohexene are the major products obtained in the absence of water, and these presumably arise from the free-radical reactions illustrated in Figure 7. This competition between free-radical and ionic reaction paths in SCW occurs frequently for heteroatom containing organic compounds. This competition and the “tunability” of the properties of SCW afford the opportunity to engineer the reaction medium to favor whichever reaction is desired. Katritzky et al.[69,70] also provide information about the effect of added formic acid (to promote acid-catalyzed reactions) and sodium formate (to promote base-catalyzed reactions) on the decomposition of these compounds in SCW.

Although diphenylmethane itself is stable in SCW, the aryl–alkyl C–C linkage in dihydroxydiphenylmethanes can be cleaved in SCW.[47] The major products are phenol and cresol in about 40% yield from reaction at 430 °C for 1 h.

Ethyl benzilate ($Ph_2COHCO_2C_2H_5$) was completely converted to other products by reaction in pure SCW at 400 °C for 30 min.[75] The main pathway was hydrolysis of the ester functionality to ethanol and benzylic acid. The acid underwent decarboxylation and eventually formed benzophenone and diphenylmethane as stable products. The addition of $ZnCl_2$ to the reactor led to cracking reactions and higher yields of single-ring products such as toluene and benzene.

e. Compounds with Two Heteroatoms. Only a few compounds recently studied under SCW conditions contain more than one heteroatom. Results from some of these have already been reviewed in one of the preceding sections. For example, most of the compounds with nitro (NO_2) substituents were included with the nitrogen-containing compounds. The one exception is nitrophenol, which is discussed in the context of other phenols in the section on oxygen-containing compounds.

One compound with both sulfur and nitrogen functionalities has been examined.[78] 2-(methylthio)-benzothiazole formed primarily aniline and benzothiazole during decomposition in SCW at 400 °C for 5 h, but it formed primarily benzothiophene during neat pyrolysis under otherwise identical conditions. These authors[78] also report results for the decomposition of a sulfur- and oxygen-containing compound, thiochroman-4-ol.

Katritzky et al.[70] examined the decomposition of oximes and *N*-oxides in SCW at 460 °C. Benzophe-

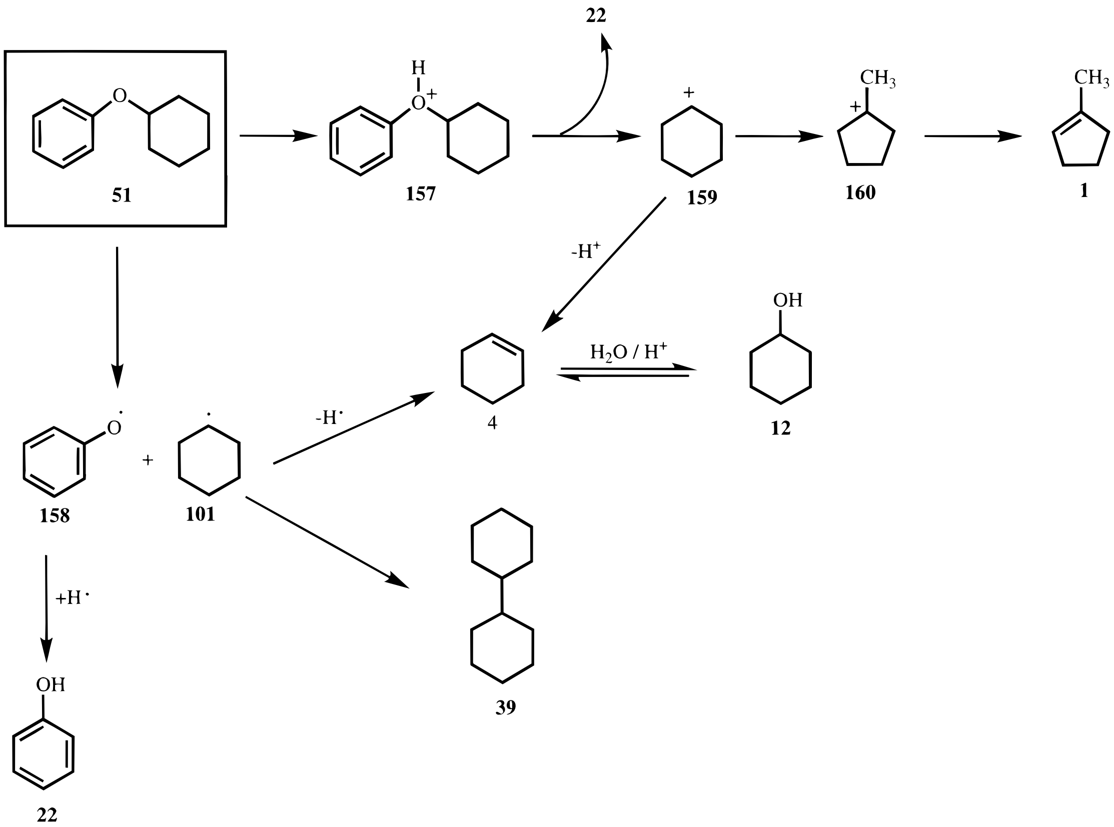

Figure 7. Key reaction steps for decomposition of cyclohexyl phenyl ether in SCW. (Reprinted from ref 69. Copyright 1994 American Chemical Society.)

none oxime underwent complete conversion after reaction in pure SCW at 7 min, and benzophenone was the major product, with 94% yield. Fluorenone oxime behaved similarly. Isoquinoline *N*-oxide was very reactive in pure SCW, with 97% conversion to essentially isoquinoline being observed after 7 min. Pyridine *N*-oxide behaved similarly.

f. Chlorine- and Fluorine-Containing Compounds. Houser and Liu[83] examined the decomposition of 1-chloro-3-phenylpropane, 2-chlorotoluene, and 4-chlorophenol in SCW. Dechlorination occurred in all cases. In addition to identifying and quantifying reaction products, they also examined the role of different reactor materials in the reactions. One of their key results is that the chloride (or HCl derived from it) attacked the metal walls of the reactor to produce metal chlorides. These compounds acted as catalysts for the decomposition reactions. In fact, both the metal walls and the metal salts had a catalytic effect on the reaction. Using Vycor inserts in the reactors dramatically reduced the reaction rates, consistent with the proposed catalysis by metals.

Elimination of halogen atoms was also evident during the processing of 1,1,2-trichlorotrifluoroethane (CFC113) in SCW. This compound underwent nearly complete dechlorination and about 90% defluorination by reaction in SCW at 400 °C and 500 bar for 100 min.[84] Trichloroacetic acid decomposed completely to HCl, CO, CO_2, and H_2 in pure SCW at 600 °C and 65 s reaction time in the absence of an added oxidant.[34] Hydrolysis was thought to be at least partially responsible for the conversion. Trichloroethylene was also susceptible to decomposition, and CO and CO_2 were the main products observed.

The most thorough study regarding the decomposition of a halogenated compound in SCW has been the recent work of Marrone, Tester, and colleagues[85−87] on the reactions of methylene chloride. The hydrolysis reaction network is as follows:

$$CH_2Cl_2 + H_2O = CH_2O + 2\ HCl$$

$$CH_2O = CO + H_2$$

$$CO + H_2O = CO_2 + H_2$$

The hydrolysis reaction (to form formaldehyde and HCl) occurred readily in subcritical water, but it was much slower in supercritical water. The authors explained this slowing down of the reaction as the temperature increased by recognizing that the dielectric constant of water decreases considerably as one increases the temperature. The dielectric constant of the reaction medium influences the rate of hydrolysis because this S_N2 reaction involves charged or polar species as reactants or intermediates. Accordingly, a medium with a higher dielectric constant will better stabilize the intermediates and hence promote the hydrolysis reaction. Marrone et al.[87] developed a quantitative kinetics model based on these arguments and showed that it accurately described the experimental data.

B. Oxidation

Oxidation of organic compounds is the chemistry in a supercritical water medium that has undoubtedly received the most attention. This chemistry forms the basis for a waste treatment technology known as supercritical water oxidation (SCWO). The technology takes advantage of the complete miscibility of organic compounds and oxygen with SCW so that there is a single fluid phase at reaction conditions. Moreover, the temperatures are sufficiently high (400−600 °C) that intrinsic reaction rates are rapid and essentially complete conversion of organic carbon to CO_2 occurs on the time scale of a few minutes. Several news reports[88−91] appeared in the past few years that describe applications and developments of SCWO technology.

1. Technology Developments

The recent literature contains many reports of process development work related to SCWO technology. These studies have provided new information about the treatability of different wastes by SCWO, and they have made advances in several engineering aspects of the technology. The process technology rather than the chemistry was the focus in these reports, so we mention them only briefly here. The interested reader should consult the overview articles by Gloyna and Li[92,93] and Levec[94] for more details on the engineering aspects of SCWO.

Much of the financial support for SCWO research and development in the United States has been from the U.S. Department of Defense, which is interested in technologies for safely treating hazardous military wastes such as energetic materials and chemical weapons. General Atomics is one of the Defense Department contractors, and they have reported[95] on the efficacy of SCWO for treating different chemical weapons agents. They have also done extensive corrosion testing and found that platinum and titanium performed the best under the harsh SCWO conditions in the presence of halides. Other groups have also examined the issue of corrosion in the SCWO environment.[96−101]

A team at Los Alamos National Laboratory has demonstrated[34] the treatability of concentrated chlorinated hydrocarbons by SCWO. To combat the corrosive conditions that would exist, they used a titanium reactor and added sodium bicarbonate to neutralize the HCl generated during processing. They also operated at high pressures (650 bar) so that the NaCl produced would remain in a fluid phase and not deposit on the reactor walls. Casal and Schmidt[102] took a different approach for destroying chlorinated hydrocarbons. They used a ceramic vessel to confine the reaction medium and a separate stainless steel pressure vessel to withstand the high pressures. The gap between the reactor and the pressure vessel was filled with water, which served as the coupling medium.

There have been recent investigations into the treatment of ion-exchange resins from nuclear power plants,[49] solid particulates,[103] dioxin-contaminated fly ash,[104] contaminated soils,[105] and different types of sludges[106−111] by SCWO. Indeed it appears that sludges are one of the complex wastes for which SCWO might be best suited. The organic content is usually high enough that auxiliary fuel is not needed, and existing treatment processes such as incineration or landfilling require expensive and at times difficult dewatering steps. SCWO has been shown to be effective for pulp and paper mill sludges,[106,107] and the economics appear to be attractive relative to incineration but not always so in comparison to landfilling. Sludges from municipal wastewater treatment facilities have also been treated.[108−111] SCWO produces a clear and odorless aqueous effluent and a settlable ash. Thus it offers a tremendous reduction in the mass or volume of the original sludge in a single unit operation. Oxidation at subcritical conditions is also used, but the reactor effluent contains organic compounds that must undergo a subsequent biological treatment.

One final class of engineering investigations that have been published recently are related to chemical reactor operation and performance. The feed characteristics required for autothermal reactor operation have been delineated.[112] It has been determined that rapid preheating of the SCWO reactor feed stream is advantageous for some wastes.[113] This rapid preheating apparently avoids the formation of more difficult to treat material (char) via thermal reactions in the preheater line. A numerical model of a pilot-scale concentric tube reactor has been reported.[114] The model accounts for heat transfer and reaction kinetics. The flow field was taken to be that of a dispersed plug-flow reactor. The most detailed reactor models have been those of Oh and co-workers,[115,116] who used computational fluid dynamics codes to describe the flow fields in a pilot-scale MODAR vessel reactor. This coupling of results from kinetics studies with computational fluid dynamics descriptions of real reactors is likely to yield important insights into the engineering of practical reaction systems for SCWO processes.

2. Homogeneous Reactions

Previous studies of oxidation reactions in SCW can be categorized according to the reaction medium being either homogeneous or heterogeneous. Homogeneous systems are those wherein the reaction occurs in a single fluid phase. Research dealing with these single-phase systems is reviewed in this section. Previous work on solid−fluid oxidation reactions in SCW is reviewed in section III.B.3.

This section on homogeneous reactions is further divided into two subsections. The first describes recent research into the reactions of single organic compounds under SCWO conditions. The compounds were typically selected because they represent compound classes thought to be important for different waste streams that might be treated by SCWO. These compounds tend to be sufficiently large that mechanistic detail is not available. As a result the information obtained is generally global kinetics, reaction networks, and the identities and yields of the products of incomplete oxidation. The second subsection describes research into the reaction mechanisms operative during SCWO. Simpler compounds such as H_2 and CH_4 are used in these studies.

a. Model Compounds. Different classes of organic compounds have recently been subjected to SCWO conditions. These include alkanes,[110] aromatics,[110] phenols,[117−124] other oxygenates,[110,117,125−130] chlorocarbons,[33,34,117,131,132] and nitrogen-containing compounds.[73,74,110,133−135] This section reviews these studies and highlights the more thorough reaction investigations.

i. Phenols. Phenol and substituted phenols are the model pollutants that have received the most scrutiny in the SCWO reaction environment. This attention is warranted because wastewaters from diverse industries often contain large amounts of phenolic compounds.

The global oxidation kinetics and reaction network for phenol has been examined by at least four different groups.[118,119,122,124] All four groups agree that the rate of phenol disappearance is essentially first order in phenol and that the rate is sensitive to the concentration of oxygen. Additionally, Krajnc and Levec,[119] Gopalan and Savage,[118] and Oshima et al.[124] concur that the global reaction order for oxygen is about 0.4−0.5, and Gopalan and Savage found the reaction order for water to be about 0.4. Koo et al.,[122] on the other hand, reported that the effect of oxygen on the rate was better modeled by saturation kinetics and that the water reaction order was 1.38. The most noteworthy aspect of the work of Koo et al. is that they were the first to distinguish between the effect of pressure and water density on the apparent oxidation rate. They found that the rate was insensitive to pressure increases at constant water density, but very sensitive to increases in the water concentration at constant pressure. All previous investigations changed the water density by changing the system pressure. Koo et al., on the other hand, added a presumably inert component (He) to the reactor to effect changes in water density without changes in the total pressure. Rice and Steeper[117] also provide some limited data on SCWO of phenol.

Products of phenol oxidation in SCW include dimers (e.g., phenoxyphenols, biphenols, dibenzofuran), single-ring compounds (e.g., hydroquinone), ring-opening products (e.g., maleic acid, glyoxylic acid, acetic acid, and other organic acids), and gases (e.g., CO, CO_2). Figure 8 shows a reaction network for phenol oxidation that illustrates the formation and destruction paths for these different compound classes.

Martino and Savage[120,121] reported on the oxidation of $-CH_3$ and −CHO substituted phenols in supercritical water. They developed a global rate equation for *o*-cresol oxidation under diverse conditions, but their kinetics analyses for the other compounds were confined to 460 °C. The focal point of the work was in comparing the reactivity of different compounds rather than in studying the reactivity of a single compound in detail. They found that the order of reactivity for both substituted phenols was in the order ortho > para > meta. Moreover, the −CHO substituted phenol was always more reactive than the otherwise identical $-CH_3$-substituted phenol. Both of the substituted phenols were more reactive than phenol itself, however. They proposed the reaction network in Figure 9 as a summary of the important reaction paths during the oxidation of these compounds in SCW.

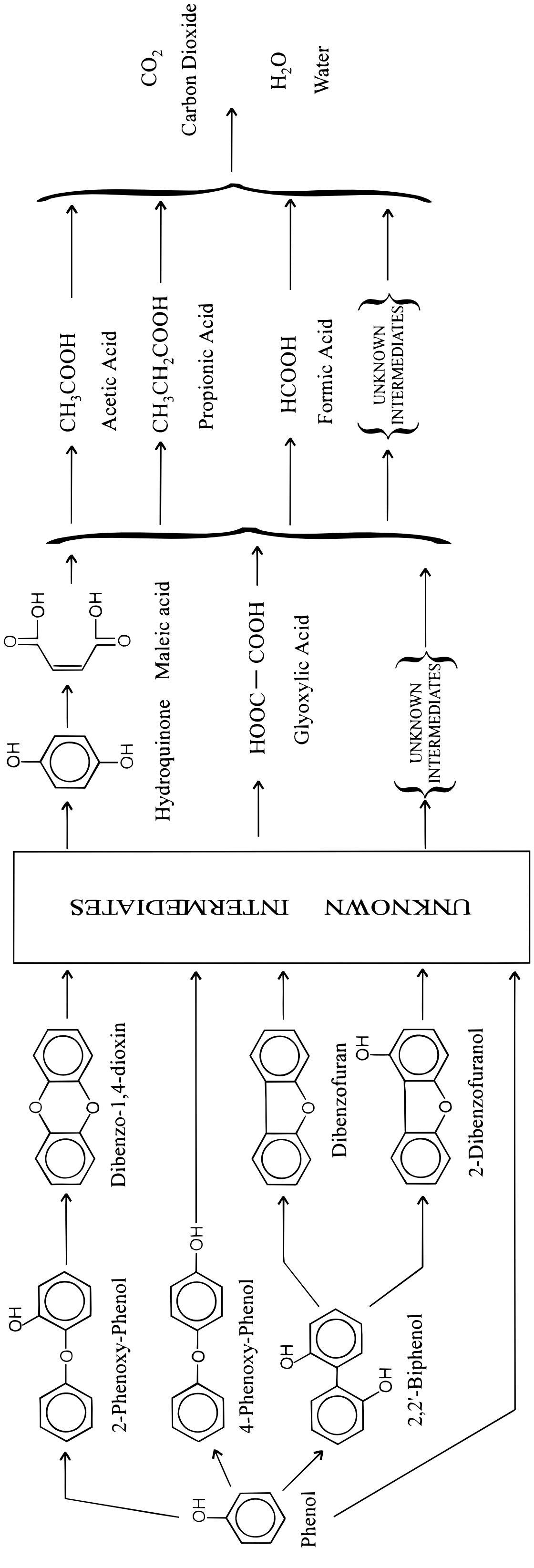

Figure 8. Reaction pathways proposed for phenol oxidation in SCW (From ref 119). (Reproduced with permission of the American Institute of Chemical Engineers. Copyright 1996 AIChE. All rights reserved.)

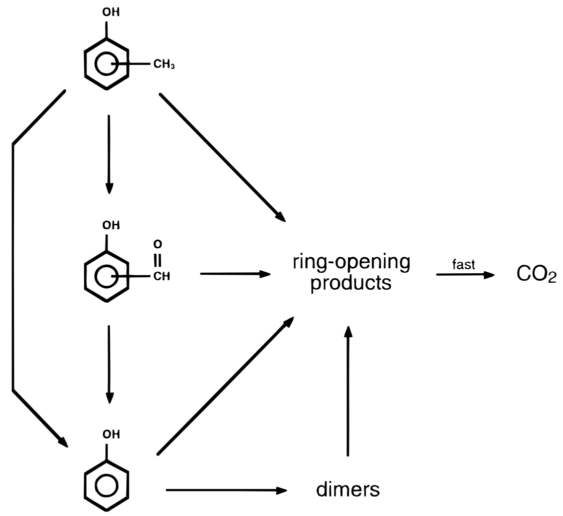

Figure 9. Reaction network for oxidation of CH_3- and CHO-substituted phenols in SCW. (Reprinted from ref 121. Copyright 1997 American Chemical Society.)

The oxidation of hydroquinone (formally an −OH-substituted phenol) has recently been studied in SCW.[123] The authors found that *p*-benzoquinone is the principal intermediate product formed. They also observed that the *p*-benzoquinone yield was higher and the CO_2 yield lower for identical residence times at supercritical conditions as opposed to subcritical conditions. The water density and the reactant concentrations were lower at supercritical conditions, however, and the effect of concentration and the water density on the oxidation rate might explain this observation.

ii. Other Oxygenates. Ethanol, 1- and 2-propanol, and 2-butanol have all been oxidized in SCW.[110,125,127] One report[125] provides rate data for the oxidation of these alcohols in mixtures, at times also with acetic acid. These experiments provide an opportunity to discern kinetic interactions that can occur during SCWO and to validate mechanism-based kinetics models. These authors used a lumping strategy whereby each elementary reaction was assigned to one of eight unique reaction families. The kinetics of each family was then assumed to follow an Evans−Polanyi relation. The mixture data were used to tune a few model parameters, but most of the parameters were determined from experiments with single-component oxidation.

2-Propanol oxidation in SCW was subsequently studied[127] in much more detail. The principal intermediate product was acetone, which formed in yields approaching 50%. Of course, the acetone product was also subject to oxidation. The authors found that a first-order reaction network of 2-propanol → acetone → oxidized products provided a good description of the experimental data.

Acetic acid oxidation in SCW has been the subject of several different kinetics studies during the last four years. Meyer et al.[126] examined the kinetics and products at high temperatures (426−600 °C), Krajnc and Levec[128] explored intermediate temperatures (420−470 °C), and Smith and Savage[129] performed experiments at lower temperatures (380−440 °C). Each of these three studies found that the global rate of acetic acid disappearance was nearly first order in acetic acid and between 0.3 and 0.6 order in oxygen. Experiments[126] at 550 °C and different water densities revealed a modest increase in the rate with increasing water density. Given the uncertainty in the data and the small range of water densities explored (less than a factor of 2), however, it is difficult to draw definitive conclusions. A much stronger effect of water density was evident in the low-temperature experiments.[129] Here, the global reaction rate was found to be second order in the water concentration. The major products from acetic acid oxidation were CO, CO_2, CH_4, and H_2. Finally, we note that Lee[130] found the kinetics of acetic acid oxidation in SCW to be sensitive to the nature of the reactor surface. More specifically, he reported that the addition of stainless steel chips to his stainless steel batch reactor accelerated the reaction rate.

Holgate et al.[56] examined glucose oxidation in SCW. They argued that glucose, the main hydrolysis product of cellulose, is a good model compound for sludge because sludges have a high fiber content, most of which is cellulose. Conversions were nearly complete in all of the experiments, and CO_2 was always the product present in highest yield. The product distribution was sensitive to the temperature used in the experiment, however. At temperatures around 450 °C there were comparatively high yields of organic acids, aldehydes, and ethylene. At 600 °C, however, these products were no longer evident, and the most abundant carbon-containing products were CO_2 and CH_4. The authors concluded that the decomposition of glucose proceeds through three kinetic regimes: (1) rapid hydrolysis/oxidation to form two- or three-carbon atom intermediates, (2) slower decomposition of these intermediates to form light gases such as methane and ethylene, and (3) oxidation of the light gases to ultimately produce CO_2 and H_2O.

More limited experimental studies of acetic acid, methanol, ethylene glycol, and methyl ethyl ketone SCWO at higher concentrations have also been recently reported.[117]

iii. Chlorinated Hydrocarbons. As noted earlier in this review, chlorinated compounds typically eliminate chlorine atoms under SCWO conditions. Chloride ion in solution leads to a corrosive environment, which complicates the effective treatment of chlorocarbons by SCWO.

In the presence of an oxidant (H_2O_2), CO_2 was the only major carbon-containing product detected from the oxidation of trichloroethylene and trichloroethane.[34] All chlorine appears as chloride ion in solution. Limited data on methylene chloride,[117] 1,1,1-trichloroethane,[117] and 3-chlorobiphenyl[131] SCWO are also available.

A more detailed kinetics study[33,86] has been completed for methylene chloride in SCW. Both hydrolysis and oxidation occur under SCWO conditions, and the rates are comparable. The chief effect of the added oxidant is to shift the product distribution to more CO and CO_2 and less CH_2O, CH_3OH, and H_2. The reaction network proposed involves three global pathways: (1) hydrolysis of CH_2Cl_2 to yield formaldehyde or methanol plus HCl, (2) oxidation of formaldehyde or methanol to CO, and (3) oxidation of CO to CO_2.

The oxidation of 2,4-dichlorophenol has been examined in SCW.[132] The disappearance rate was reported to be nearly first-order in both the chlorophenol and in oxygen, but none of the experimental data were reported. The reactions were reportedly accomplished in a batch reactor for 5−10 min at temperatures between 673 and 873 K. If these reported reaction conditions are correct, then this compound appears to be surprisingly less reactive than related phenolic compounds. These authors also found that the presence of Fe^{3+} and Na^{+} ions in solution enhanced the conversion and suppressed byproduct formation.

iv. Nitrogen-Containing Compounds. Lee and coworkers examined the decomposition of nitrobenzene[73] and 4-nitroaniline[74] in supercritical water. Nitrobenzene decomposed even in the absence of oxygen, but in the presence of oxygen the decomposition rate is faster. The products of incomplete oxidation included aniline, phenol, 2-(2-pyridinyl)-benzonitrile, and dibenzofuran. The authors concluded that most of the nitrogen appears as N_2 in the reaction products. 4-Nitroaniline contains both an NO_2 group, which is a potential oxidant, and an NH_2 group, which can be further oxidized. The rate of SCWO was independent of the oxygen concentration, but 0.85 order in nitroaniline and −0.9 order in water.

Buelow and co-workers[133−135] examined nitrogen speciation and the efficacy of nitrate and nitrite as oxidants in SCWO. They showed[135] that reactions between NH_3 and MNO_3, where M is monovalent cation (Na, Li, H), converted nitrogen largely to N_2, with lesser amounts of N_2O and NO. This chemistry can provide an effective nitrogen control strategy for SCWO. The authors also reported the kinetics for these reactions and they postulated mechanisms. Moreover, nitrate and nitrite were shown[133,134] to be effective oxidants for organic compounds as well as for NH_3.

b. Mechanisms. There has been considerable effort expended on elucidating the reaction mechanisms operative during SCWO. One working hypothesis, which appears to be largely valid, is that homogeneous SCWO chemistry is analogous to free-radical gas-phase oxidation chemistry in the same temperature regime. If this hypothesis is correct, one can use the vast gas-phase combustion kinetics database for elementary reaction steps to develop quantitative, predictive, mechanism-based reaction models for SCWO. Such an approach could accelerate our understanding of the fundamentals of SCWO chemistry and at the same time provide a firm basis for reliable engineering process models.

Adapting gas-phase combustion models to develop quantitative, mechanism-based kinetics models for SCWO requires that one account for the effect of high pressures and high water densities on the rates of unimolecular reactions and other reactions with pressure-dependent rates. One should also account for fluid-phase nonidealities when calculating chemical equilibrium constants.

Nearly all of the mechanistic studies completed to date have (understandably) dealt with simple compounds such as H_2, CO, CH_4, and CH_3OH, for which the gas-phase combustion mechanisms are relatively small and well established. One exception is the work of Gopalan and Savage[136,137] on developing a mechanism and model for phenol oxidation in SCW.

Validation of a proposed mechanism and set of rate constants and thermochemical data requires comparison with experimental measurements. To this end, there have been recent experimental studies of the SCWO of H_2,[138] CO,[138] CH_4,[139,140] and CH_3OH.[141,142] The data available include reactant conversions and product yields as functions of residence time, temperature, and species' initial concentrations. These experimental investigations are all accompanied by a complementary mechanistic modeling component. There have also been accounts of exclusively modeling studies[143−149] of previously published data.

To date, SCWO mechanistic models have been validated by comparing their predictions with experimental measurements of the yields of stable molecular products. Improvements in mechanistic models can be achieved by also comparing model predictions with experimental measurements for reactive intermediate molecular and free-radical products. These measurements would need to be made in situ, and to date there have been no reports of measuring radical concentrations during SCWO processing. Croiset and Rice,[150] however, have recently reported the direct measurement of H_2O_2 by Raman spectroscopy during SCWO of simple alcohols. They found that the measured H_2O_2 concentration was lower than that predicted by detailed chemical kinetics models. There have been several other reports of in situ measurements of chemical species (molecules and ions) in near-critical and supercritical water. The techniques developed include fiber-optic Raman spectroscopy,[151,152] Fourier transform infrared (FTIR) spectroscopy,[153−156] and emission spectrometry, which has been used in high-pressure diffusion flames.[157]

The SCWO mechanisms proposed recently for simple compounds are all chemically similar, and they typically comprise on the order of 100 individual elementary reaction steps. The main differences in the quantitative predictions of the models can be traced to the values of the rate constants for a few elementary reactions, the standard heats of formation of a few chemical species, and the treatment of the effect of pressure on the rates of a few chemically activated reactions. Although the quantitative details may differ, all of the mechanistic modeling work is qualitatively consistent in pointing out essentially the same major reaction paths for the oxidation of C_1 compounds and H_2 in SCW. For example, Figure 10 shows the major reaction paths for the oxidation of CO and H_2 in SCW.

Sensitivity analyses performed on these mechanism-based models have revealed that the calculated conversions and product yields are very sensitive to only a remarkably small number of elementary reactions. Some of these reactions are reactant

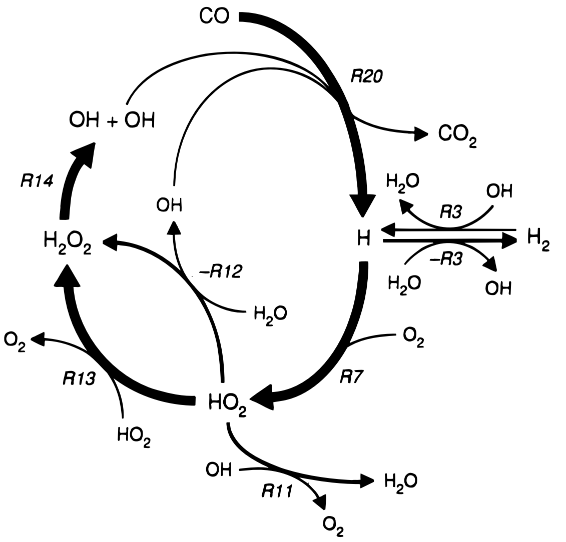

Figure 10. Major free-radical reactions for CO and H_2 oxidation in SCW. Arrow thicknesses indicate relative rates of reaction. (Reprinted from ref 138. Copyright 1994 American Chemical Society.)

specific (e.g., OH and HO_2 attack on the hydrocarbon reactant), but several elementary steps appear to be important for the oxidation of nearly any organic compound in SCW. These steps are $H_2O_2 = 2\ OH$, $2\ HO_2 = H_2O_2 + O_2$, $OH + HO_2 = H_2O + O_2$, and $H_2O_2 + OH = H_2O + HO_2$. An improved knowledge of the kinetics of these steps under SCWO conditions and the thermochemistry of the species involved, especially HO_2, would lead to more reliable mechanism-based models for SCWO.

There has been some significant recent progress in the measurement of the rates of elementary reactions in SCW. Recognizing the sensitivity of the results of SCWO mechanistic models to the kinetics for H_2O_2 decomposition into two OH radicals led Croiset et al.[158] to measure the rate of this reaction in SCW up to 450 °C. The analysis was complicated by the presence of surface-catalyzed reactions and a multistep decomposition mechanism. Nevertheless, these investigators were able to measure the rate constant for this important reaction. Their measured value is higher than the recommended[159] value of the high-pressure limit rate constant for this reaction in the gas phase. Croiset et al. found that the new, higher value improved the predictions of their mechanistic model for methanol SCWO. Interestingly, however, Dagaut et al.[144,145] had previously found that they needed to reduce the value of this rate constant below its recommended high-pressure limit to obtain agreement between their model and published experimental data for simple compounds.

Ferry and Fox[160] very recently provided kinetics for the self-reaction of the hydroxycyclohexadienyl radical in SCW. This radical was formed from the addition of OH radical to benzene in a pulse radiolysis experiment. These investigators also examined the competition between OH addition and one-electron oxidation in SCW for different substituted phenolate anions. Additional work with pulse radiolysis in SCW is needed to measure the rates of important elementary reactions, such as OH + fuel, for SCWO.

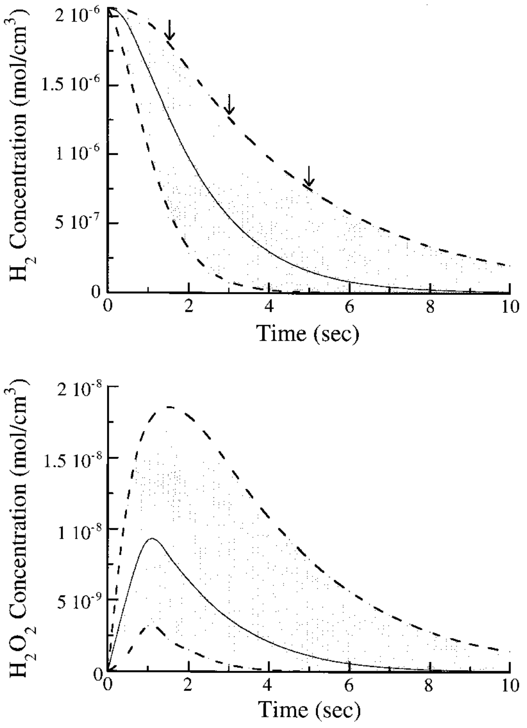

Figure 11. Effect of parametric uncertainty on concentrations of H_2 and H_2O_2 calculated by a mechanism-based kinetics model for H_2 oxidation in SCW at 823 K. The solid curve is the median predicted value, and the shaded area contains 95% of the predicted concentration values. From ref 149. Reprinted by permission of Elsevier Science from "Incorporation of Parametric Uncertainty into Complex Kinetic Mechanisms: Application to Hydrogen Oxidation in Supercritical Water," by Phenix, B. D.; Dinaro, J. L.; Tatang, M. A.; Tester, J. W.; Howard, J. B.; McRae, G. *J. Combustion and Flame* **1998**, *112*, 132−146. Copyright 1998 by The Combustion Institute.

Each of the parameters (rate constants, thermochemical data) in mechanism-based detailed chemical kinetics models for SCWO has an associated uncertainty. Two recent reports have examined how this parametric uncertainty is manifested in the predicted reactant conversions and product yields for SCWO of H_2[149] and methanol.[147] These studies show that there is considerable uncertainty in these model calculations. For example, Figure 11 shows the median value and the 95% confidence region for model calculations for SCWO of H_2. Most of the uncertainty in these calculations can be attributed to the uncertainties in just two parameters, the forward rate constant for $H_2O_2 = 2OH$ and the standard heat of formation for the HO_2 radical. Given the uncertainties in the model predictions and in the experimental data used for model validation, Brock et al.[147] concluded that their mechanism-based kinetics models was consistent with SCWO experiments for methanol. Thus, the working hypothesis that gas-phase combustion chemistry can be adapted to model homogeneous SCWO chemistry appears to be reasonable.

When doing this type of mechanistic modeling work, however, one must be careful to consider possible effects of water molecules on the structure and energetics of transition states for elementary reactions. It is possible that the transition state for a reaction in water is different than the transition state for that reaction in the gas phase. Formic acid decomposition provides one example.[82] The water–gas shift reaction ($CO + H_2O = CO_2 + H_2$) is a second example. The rate of this reaction in SCW[161] is extremely sensitive to the water density. About a 5-fold increase in the density at 450 °C resulted in about a 100-fold increase in the apparent first-order rate constant. This qualitative effect of water on the rate was previously predicted by a quantum chemical calculation, which showed that water molecules participated in the transition state, and thereby influenced the rate of reaction.

3. Heterogeneous Reactions

The desire to reduce the severity of the processing conditions of SCWO and thereby improve the economics has motivated much recent research into ways to enhance the oxidation rates. One approach[162] is to add "rate enhancers" such as H_2O_2 or HNO_3, which are more powerful oxidants than O_2 and can more rapidly initiate the free-radical chain oxidation reactions in the fluid phase. A second approach is to use homogeneous oxidation catalysts, and a third is to employ heterogeneous catalysts. It is this third option that we consider in this portion of the review.

Catalytic oxidation in supercritical water is the subject of a thorough review by Ding et al.[163] They summarize the relatively small number of actual catalytic oxidation studies in SCW that had been conducted up to that time (early 1996), but more importantly, they place catalytic SCWO in the context of other catalytic oxidation technologies. They also delve into the important issues of catalyst hydrothermal stability, activity, and preparation. For example, Cr_2O_3 is not a good SCWO catalyst because Cr_2O_3 is not stable in SCW, and the chromium can be leached out of the catalyst.[164] Loss of catalyst and the presence of toxic chromium in the process effluent are both problematic.

Some studies in this area are surveys wherein different potential catalysts and different organic reactants were used. For example, Krajnc and Levec[165] reported that a copper oxide/zinc oxide catalyst provided substantially higher conversions and higher selectivities to CO_2 (than uncatalyzed SCWO) for the oxidation of alcohols, acetic acid, methyl pyrrolidone, benzoic acid, and phenol. Ding et al.[166,167] reported similar observations for the oxidation of benzene, phenol, and dichlorobenzene over Cr_2O_3, V_2O_5, and MnO_2 catalysts.

The more recent reports tend to be more focused on a single compound and single catalyst combination. These studies have examined several specific systems in detail so that reaction rate laws and information about the catalyst stability and activity maintenance are available. Systems investigated include pyridine[168] and NH_3[169] over a commercial MnO_2/CeO_2 catalyst, phenol[170] and acetic acid[128] over a proprietary copper/zinc/cobalt oxide supported catalyst, and phenol[171] over a commercial manganese and copper oxide supported catalyst. In all cases, the presence of the catalyst greatly accelerated the rate of disappearance of the target compound and the conversion of organic carbon to CO_2. The catalyst also reduced the yield of organic byproducts. Figure 12 shows representative results. This enhanced reaction rate and selectivity at milder reaction conditions continues to motivate research into catalytic SCWO, which appears to offer a route to improved SCWO process economics.

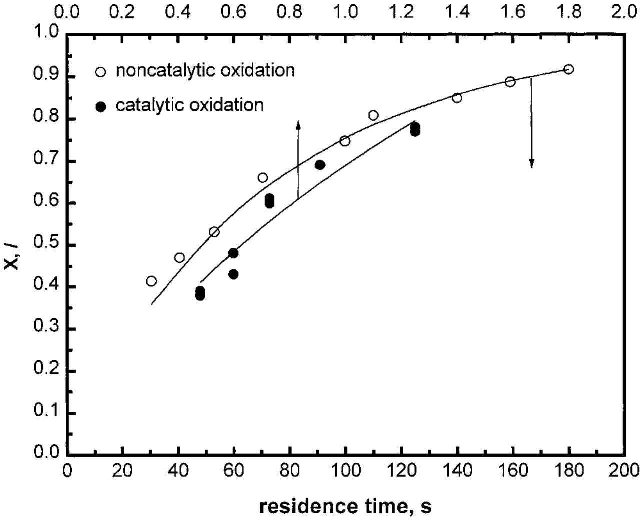

Figure 12. Comparison of catalyzed and uncatalyzed oxidation of phenol in SCW at 400 °C. The conversions are comparable, but the time scale for uncatalyzed oxidation is 2 orders of magnitude longer. (Reprinted from ref 170. Copyright 1997 American Chemical Society.)

IV. Summary

This comprehensive review is the first to be dedicated exclusively to the topic of organic chemical reactions in supercritical water. The review dealt with the three broad areas of research in this field, namely chemical synthesis, decomposition of organic materials and compounds, and complete oxidation. Over half of the articles cited in this review dealt with the last application, supercritical water oxidation. About 25% dealt with the conversion of organic materials by processing in supercritical water, and only about 15% of the articles cited in the review dealt with chemical synthesis. Given the limited work done to date on chemical synthesis in supercritical water and the current interest in and importance of environmentally benign chemical processing, the area of chemical synthesis in high-temperature water is the one that will grow most rapidly. There are simply vast expanses of uncharted territory in this field, but there has also been sufficient exploratory work that some guidance is available.

This review showed that there is a broad range of chemical transformations that can be effected in the nonconventional reaction medium of supercritical water. These transformations include hydrogenation, carbon–carbon bond formation, dehydration, decarboxylation, hydrodehalogenation, partial oxidation, and hydrolysis. The rates and selectivities of these different reactions can be manipulated by judicious selection of temperature, pH, catalyst, and water density, so that one can thereby control the functional group transformations in SCW. Some of the knowledge required to make these "judicious selections" has been elucidated, but much more work remains to be done if SCW is to become a medium routinely considered for synthetic organic chemistry. One type of study needed is additional investigations that demonstrate in SCW chemistries that are used routinely in organic solvents. This is the type of study that has most often been done in this field. In addition, the field could progress in even larger steps if new chemistries and new catalysts were developed specifically for high-temperature water systems. Aside from the type of pioneering exploratory research mentioned above, there is a genuine need for careful quantitative studies of the reaction kinetics and mechanisms for chemistries that have already been demonstrated in SCW. For example, studies that resolve the reaction networks and determine how the rates of the different paths vary with the process variables (concentrations, temperature, pressure) would facilitate the conceptual design and analysis of chemical processes based on SCW reaction media.

Cases discussed in this review show that water near its critical point can serve as a solvent, a reactant, and a catalyst. In the case of acid- or base-catalyzed reactions, the catalytic role is due to the elevated value of K_w in subcritical water which leads to higher concentrations of H^+ and OH^- in solution. In other cases, the catalytic role is more subtle and can involve participation of water molecules in transition states for elementary reactions. There is a need for even more studies that resolve the specific role(s) of water in chemical reactions in SCW. These studies should take advantage of in situ measurements of reactants and reaction intermediates. Advances can also be made by using molecular simulation and computational chemistry to investigate molecular-level details that are experimentally inaccessible.

This field of organic chemical reactions in supercritical water will continue to advance as scientists and engineers creatively exploit the unique and adjustable properties of SCW and seek environmentally benign chemical processes.

V. Acknowledgments

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